



# TiO<sub>2</sub> for water treatment: Parameters affecting the kinetics and mechanisms of photocatalysis

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## ABSTRACT

The photocatalytic activity of TiO<sub>2</sub> is the result of an interplay between a considerable number of parameters, e.g., phase composition, electronic structure, particle size, exposed surface area, degree of aggregation, mobility of charge carriers, presence of impurities, amount and kind of defects, adsorption of molecules from gas or aqueous phase, lateral interactions between adsorbed species, nature of solvent, etc. Furthermore, these parameters can be broadly subdivided into those that are intrinsic to the photocatalytic material, and those that are extrinsic being influenced by the surrounding environment and conditions. The specific function and influence of a given feature for the photocatalytic performance of a TiO<sub>2</sub> sample is difficult to characterize since many of the before-mentioned parameters are strongly coupled. For example, while the degree of aggregation could be inherent to a given material, it is also simultaneously influenced by pH. The degree of aggregation can then influence adsorption of molecules, light scattering and photon adsorption, charge carrier dynamics etc. The plurality of variables driving the nature of the photocatalytic activity, presents a challenge when trying to understand the kinetics and mechanisms underlying photocatalytic processes. It is of primary importance to develop a method to understand and control these properties (or at least some of them). In this paper, we also discuss the relevance of quantum-integrated systems in which the local environment where the molecule is adsorbed is different from the “lonely” photocatalyst or the molecule in solution, and could be treated as a whole.

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## 1. Introduction

Photocatalysis using semiconductor particles has found increasing interest to solve global pollution problems, and has been proven to effectively degrade a great number of pollutants. Compared to other semiconductor photocatalysts, TiO<sub>2</sub> has so far been shown to be the most promising material used for both fundamental research and practical applications because it is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable. Although the detailed mechanism of photocatalysis varies with different pollutants, it is commonly agreed that the primary reactions responsible for the photocatalytic effect are interfacial redox reactions of electrons and holes that are generated when the semiconductor catalyst is exposed to light of sufficient energy.

The photocatalytic efficiency can be evaluated by the measurement of the quantum yield of reaction products and is, unfortunately, usually found to be rather small. In fact,

time-resolved spectroscopic studies reveal that most of the photogenerated e<sup>-</sup>/h<sup>+</sup> pairs (~90%) recombine rapidly after excitation. This is assumed to be one reason for the relatively low quantum yield (<10%) of most semiconductor-based photocatalytic reactions.

In the simplest scenario of UV illuminated TiO<sub>2</sub> suspensions, the oxidative part is attributed to adsorbed or free hydroxyl radicals created from the dissociated adsorption of water at the TiO<sub>2</sub> nanoparticles. Such radicals can further react with the pollutant present in the system yielding a variety of degradation compounds according to the nature of the pollutant. In the case it is degraded into minimal moieties, carbon dioxide is obtained and the process is called mineralization or photomineralization. Accounting for the reductive part, molecular oxygen dissolved in the solution may be converted into water. An alternative scenario is described by the direct hole oxidation by the adsorbed pollutant. In summary, the photocatalytic oxidation can be mediated either by hole or by hydroxyl radicals. The overall oxidation pathways may differ, however both lead to similar distribution of products, therefore it has been difficult to distinguish between the two [1]. The photocatalytic reduction reaction usually involves the transfer of the conduction band electrons, as mentioned above, usually to dissolved oxygen

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in the solution. Furthermore, it is accepted that this reaction is the rate-determining step of the photocatalytic degradation process.

While on the one hand it is of importance to improve the efficiency of photocatalysis processes, at the same time, to achieve commercial viability, the expanse of available solar energy needs to be tapped to activate the photocatalytic materials cheaply. Hence, more recently, much of the research energy has been diverted into extending the photocatalytic response of the photocatalyst to the visible region. What has been observed so far is that the reaction rates achieved with these newly developed visible light photocatalysts are even lower than their UV activated counterparts. A compromise must be reached between the two, ultimately what is desired are new photocatalysts that are highly active and responsive to the visible portion of the solar spectrum.

Identifying the factors that govern the kinetics of photocatalytic processes and understanding the role that they play is inherent to achieving the desired goal. Although great strides have been made in the past 25 years, more remains unknown, making  $\text{TiO}_2$  photocatalysis an interesting challenge not only for engineers but also for fundamentalists. Both efforts are therefore necessary in the future since the interpretation of the results in kinetics studies of  $\text{TiO}_2$  photocatalytic systems for water treatment and the elucidation of the underlying mechanisms are not straightforward. The complications are mainly due to: (i) the analytical instrumentation nowadays which is often limited to a few specific systems, and to (ii) the considerably large number of parameters to take into account when designing an experiment. Hence, we intend here to offer the reader a condensed and critical overview of the work done so far. We also present an emerging, continuously growing and promising branch for detailed studies of the systems, computational-theoretical calculations by quantum chemical methods.

## 2. Elementary Steps of Photocatalytic Reactions

Kinetics involves the study of reaction rates. A fact that was recognized about photocatalytic reactions early on was that the quantum yields are low. This was identified as a bottleneck to the application of this promising technology and a large proportion of the research energy invested in photocatalytic processes has targeted the improvement of the photocatalytic activity of  $\text{TiO}_2$  photocatalysts. Another segment of research has gone into improving reactor design and optimizing reaction conditions. Only recently, with the advance in computational sciences, theoretical calculations performed to a quantum level of the systems are becoming a powerful tool for the interpretation and the understanding of the underlying mechanisms in photocatalysis.

In photocatalysis, kinetic studies are focused on the kinetics of charge carrier generation and their subsequent transfer to various reacting species. Standard chemical engineering concepts apply and just as in other heterogeneous catalytic process,  $\text{TiO}_2$  photocatalysis can be broken down into a series of steps. Charge carriers are generated upon illumination and these charge carriers can get trapped in the semiconductor, they can recombine or they can take part in various redox reactions. For a complete list of the redox reactions that take place during a typical photocatalytic reaction, refer to the work by Litter [2].

Elementary steps, which occur during photocatalytic reactions, can very generally be grouped according to whether they occur inside the catalyst or on its surface. In Figure 1 we have used a schematic to show the reaction steps that can take place during a typical photocatalytic reaction. We have included the time scale at which these reactions occur to give the reader a feel for the dynamics. This schematic will also serve as a reference when examining

parameters, which are influential on the photocatalytic reaction to highlight the reaction step at which they may play a role and their influence on the reaction kinetics. As with all heterogeneous catalysis reactions mass transfer parameters are important [3,4]. Ultrafast processes such as the generation, trapping and recombination of conduction band electrons and valence band holes occur on the femto, pico and nano time scales and interfacial surface reactions which take place on the ms and second scales.

## 3. Extrinsic and Intrinsic parameters affecting the kinetics of photocatalysis

Parameters affecting the kinetics and mechanisms of photocatalytic reactions can be broadly subdivided into ones that are intrinsic to the photocatalytic material, and those that are extrinsic, with the latter being influenced by the surrounding environment and conditions. Tentatively, the interface between the surface of the photocatalyst and the surrounding environment (be it a gas or a liquid) can be defined as the limit dividing the extrinsic and the intrinsic worlds. It is useful to look at the individual reaction steps involved in a photocatalytic reaction to identify where influential reaction parameters could play a role. All parameters influence interfacial reactions and their rates.

Intrinsic parameters, assumed to influence the dynamics of the photogenerated charge carriers include the crystallographic phase, the exposed crystal face, crystallite size, the presence of dopants, impurities, vacancies, and different surface states originating from the presence of a variety of lattice defects. Some extrinsic parameters include the pH of the solution, structure of the pollutant that can be either organic or inorganic, its initial concentration, the presence of impurities in the system, and the light intensity (photon flux). Other extrinsic parameters that can influence mass transfer include catalyst dosage and flow rate.

Some intrinsic and extrinsic parameters are strongly coupled. Therefore, the specific function and influence of a given feature for the photocatalytic performance of a  $\text{TiO}_2$  sample is at times difficult to characterize. For example, while the degree of aggregation could be inherent to a given material, it is also simultaneously influenced by pH. The degree of aggregation can then influence adsorption of molecules, light scattering and photon adsorption, and charge carrier dynamics etc. Perhaps, for parameters such as the exposed surface area and mesoporosity of a photocatalyst, the classification of intrinsic and extrinsic does not quite capture the nature of these parameters.

### 3.1. Techniques for the Study of the Parameters

Traditional kinetic experiments on photocatalytic reactions have provided tremendous quantitative knowledge about the reaction rates for a wide range of reactants under various conditions. Several groups have devoted their research activities to provide quantitative measurements on the ultrafast processes [5–9]. The use of transparent nanoparticles has allowed the use of spectroscopic methods and has provided mechanistic information on photocatalytic reactions. Transparent nanoparticles are basically small (typically < 10 nm) and very well dispersed particles. Since the degree of aggregation is very low due to the stabilization provided by the surface charges, scattering effects are minimized and transparency is achieved. Such systems are advantageous because suspensions of considerably high concentration of the photocatalyst can be prepared in very small volumes. Thus the number of electron-hole pairs created is proportionally high and the systems can be rather easily handled in different equipments and investigated by means of several techniques without the need for scaling up the experimental set ups to overcome detection limits. Fur-

thermore lies the facilitation provided for the synthesis procedures previous to the investigations, where laboratory scale amounts of photocatalyst suffice, usually without the need of repeating the entire synthesis till the required amount is obtained. Disadvantages focus mainly in the role that the surface charges may play in the system, not only directly, e.g., from the mechanistic point of view, but indirectly, interfering with the surface coverage of the adsorbant and the exchange equilibrium with the solution. Such disadvantages crucially disrupt the transfer of the acquired knowledge to other types of nanoparticles, usually commercial types, which cannot be either investigated by such techniques or transformed into those environments in order to compare results.

However, ultrafast kinetic studies continue to provide new insights into heterogeneous photocatalysts such as the role of catalyst aggregation and the occurrence of the antenna effect [10,11]. The Antenna effect is one of the few suggested mechanisms taking place upon illumination beyond the well-accepted elementary steps. According to the antenna mechanism the energetic coupling in a long chain of nanoparticles, assumed to occur by topotactic attachments, enables electron transfer from the particle where the initial photon absorption took place to another  $\text{TiO}_2$  particle within

the aggregate where the electron transfer process finally occurs [12].

Several tools are available to study ultrafast processes in illuminated  $\text{TiO}_2$ . Transient absorption spectroscopy and time-resolved diffuse reflectance (TDR) spectroscopy are two common ones. The trapped holes and electrons show broad absorption in the UV-vis region, centered around 430–520 nm and 600–800 nm. However, light scattering of larger particles (micron sized) could be problematic for such studies. Here, diffuse reflectance measurements are useful. From laser flash photolysis studies and from transient absorption measurements Bahnemann et al. have contributed greatly to the basic understanding of elementary processes in illuminated semiconductors [7,13–15]. For example Bahnemann et al [7] were the first to reveal that there are at least two different types of hole traps in excited  $\text{TiO}_2$  particles; deeply trapped holes, which are long-lived and unreactive, and shallowly trapped holes, which exhibit a high oxidation potential.

To use absorption spectroscopy to study reaction kinetics, it is necessary to clearly distinguish and assign the absorption bands of the transient species. Recently, several groups have revealed the transient absorption bands of trapped conduction band electrons in

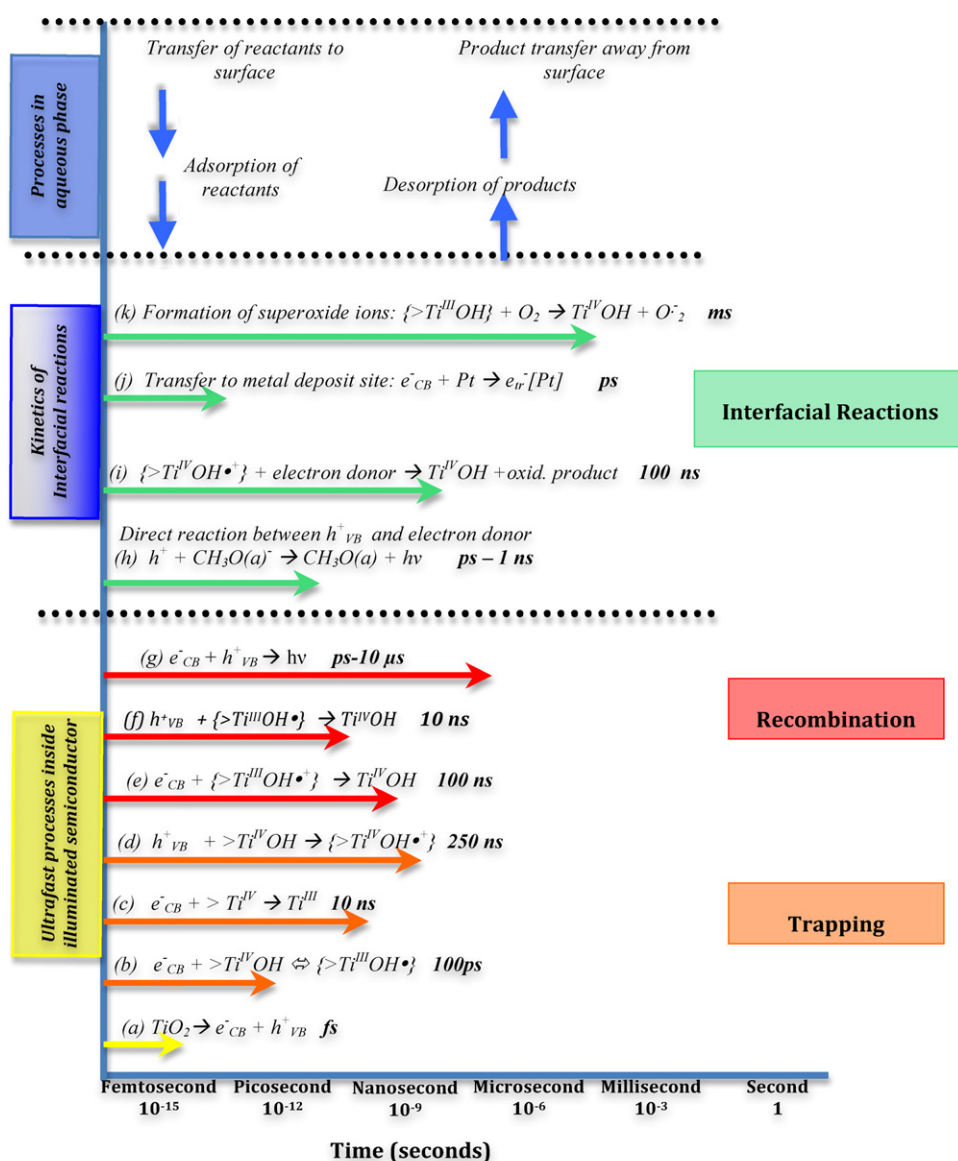


Figure 1. Elementary reactions in  $\text{TiO}_2$  photocatalysis with corresponding timescales.

the mid IR wavelength region (for example see Chen et al [16]). Due to limited interference in this region by the holes, time-resolved mid-IR absorption spectroscopy has been identified as potentially a powerful tool to accurately trace the kinetics of the electrons. Chen et al studied the photocatalytic production of  $\text{H}^+$  from methanol. They suggested that adsorbed  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  on the surface play a favorable role in the transfer of  $\text{H}^+$  (proton) on the surface of the activated  $\text{TiO}_2$ , hence promoting  $\text{H}_2$  production from methanol [16].

The generation and decay of singlet molecular oxygen ( $^1\text{O}_2$ ) were investigated by Daimon et al [17] by monitoring its phosphorescence under various conditions. Singlet molecular oxygen is formed by electron transfer processes involving the reduction of molecular oxygen to  $\bullet\text{O}_2^-$  by photogenerated electrons followed by photooxidation of  $\bullet\text{O}_2^-$  to  $^1\text{O}_2$  by the photogenerated holes. Nakoaka et al [18] used electron spin resonance (ESR) to study the effect of heat treatment on the radicals produced in  $\text{TiO}_2$  after UV illumination. They found that the degree of hydroxylation, which changes as a function of heat treatment affects the nature of the radicals that are produced. For example for powders that were not heat treated, holes were trapped at the surface forming  $\text{Ti}^{4+}\text{-O}\bullet$ – $\text{Ti}^{4+}\text{OH}\cdot$ . For the heat-treated samples, the holes were trapped as  $\text{Ti}^{4+}\text{-O}^{2-}$ – $\text{Ti}^{4+}\text{O}\bullet$  radicals at the surface. Jung et al [19] used photoluminescence measurements to also investigate the effect of heat treatment on the charge carrier generation with anatase  $\text{TiO}_2$  particles. They observed an increase in the photoluminescence intensity with an increase in calcination temperature. From this, they inferred a reduction of internal defects with increased heat treatment, which has a positive effect on photoactivity (as long as no significant rutile phase was formed).

High-resolution scanning tunneling microscopy (STM) holds a lot of promise for elucidating the mechanisms of photocatalytic reactions. However, due to the measuring conditions, e.g. the Ultra-High-Vacuum (UHV) required by the technique, the results must be used with care for the interpretation of photocatalytic phenomena of particles in contact with pollutants in the gas phase. Unfortunately, the use of such results for systems in solutions is rather limited due to the drastic change introduced by the presence of the solvent. Even though this technique cannot be used for in situ kinetics studies for water treatment, some approaches with adsorbed water molecules have provided interesting information with relevance for mechanistic studies to the atomic level of investigation (see Section 4 – quantum-integrated systems).

Recently, Mattiesen et al reported the unprecedented details of the intermediate steps for the oxidation of H adatoms by  $\text{O}_2$  molecules on a single crystal rutile  $\text{TiO}_2(110)$  surface [20], additionally they showed the significance of a H bond mediated rollover mechanism operating for the water dimers which enabled them to diffuse faster than the water monomers [21,22]. An additional comment on the use of STM is that direct investigations can be only done on single crystals while the use of nanoparticles is not possible. This raises unavoidable complications for the transfer of knowledge acquired from the single crystals to the nanoparticles. Feldhoff et al has shown that the crystallographic exposed faces of anatase nanoparticles differ from the most stable ones of the single crystals. While anatase single crystals mostly expose the (101) facet, nanoparticles ranging between 5–100 nm expose mainly the (100) facet [23].

Much remains to be understood about the mechanisms of  $\text{TiO}_2$  photocatalysis, for instance, Monllor-Satoca et al [1] proposed that the oxidizing holes are trapped at terminal  $\text{Os}^{2-}$  or protonated  $\text{Os}^{2-}$  (which can be considered as intrinsic surface states, surface hydroxyl groups). This was based on deductions made from UPS spectra of single crystal rutile (110) surfaces with adsorbed water, and their associated energy levels relative to the  $\text{TiO}_2$  valence band [24]. Such information could prove to be critical to the design of

highly active photocatalysts, and perhaps using high resolution STM, such states can be distinguished. This differs from the generally accepted idea that the holes are trapped by OH ions adsorbed on terminal Ti atoms (extrinsic surface states). With regard to this point, theoretical calculations of the exited states of adsorbed oxalic acid on anatase (100) and rutile (110) also showed that depending on the surface structure adopted by the molecule, both charge carriers can be directly generated, at least partially on the adsorbed species and the surface titania atoms to which it is bound [25].

### 3.2. Mass Transfer Parameters Influencing the Photocatalytic Reactions Rates

Theoretically, initial rates of photocatalytic reactions are directly proportional to the amount of catalyst as the number of active sites increase. However, above a certain amount of catalyst the rates level off. This is most of the time explained as being due to screening effects of the particles, which decrease the penetration depth of the UV radiation. An optimum catalyst loading depends on reactor geometry. When comparing slurry type reactors to ones in which the photocatalyst is supported, the latter has higher mass transfer limitations [2,26]. At lower solute concentrations, the photocatalytic rates in immobilized-catalyst photoreactors could be half of the rates obtained for slurry systems. In a well-mixed slurry photoreactor system, the mass transfer limitations are typically negligible; hence photocatalytic reaction mechanisms are usually based on a reaction controlled by adsorption kinetics [27]. Ballari et al [28,29] provided new insights into this field of study. Ballari et al went a step further and showed that for slurry type reactors, external interfacial mass transfer limitations would only be seen for larger particle sizes which are not typically employed in suspended form. Internal mass transfer limitations within agglomerates will almost always be present, and are mostly produced by light penetration restrictions while mass transfer limitations inside the catalyst particles are of lesser significance.

### 3.3. Processes Occurring at the Interface

#### 3.3.1. A note on L-H Kinetics

The photocatalytic reaction occurs on the surface of the catalyst and therefore a good adsorption capacity is expected to favor the reaction kinetics. Adsorption-kinetic models, and specifically the Langmuir-Hinshelwood (L-H) model, are the most commonly applied to describe photocatalytic mineralization reactions [30]. The L-H based kinetic models relate the rate of surface-catalyzed reactions to the surface covered by the substrate. According to the L-H model, the rate of a unimolecular surface reaction is proportional to the surface coverage. As the concentration of the reactants increases above a certain level however, the catalyst surface becomes saturated, and this may even lead to a decrease in the observed rates. The generation of difficult to degrade intermediates and their continued presence on the surface can also have a negative effect on the degradation rate of their parent compounds.

There are limitations to applying the L-H kinetics model [31,32], and there is a current active discussion regarding this issue [1,33–35]. Concerns include the adsorption-desorption equilibria under illumination [1,31,32]. Also of relevance here is the influence of photon flux on the kinetics [36]. Another concern about L-H kinetics is that while adsorption of organics seems to be important for efficient photocatalytic reactions, for reactions involving indirect transfer by OH radicals, this may not be necessary the case since OH radicals are able to diffuse into the solution [1,37,38]. The use of the initial degradation rate rather than the degradation rate during the whole photomineralization process, which can sometimes differ greatly, has also been questioned. Another problem is the consideration of an “unchanged” photocatalyst surface dur-



ing the reaction under illumination [39]. If the surface changes; for example due to the de-aggregation of particles, the creation of OH surface groups upon UV absorption, bond cleavage, photodesorption of co-adsorbed water, and UV-triggered substitution of strongly adsorbed impurities by the pollutant, the L-H model must be modified in order to account for these changes.

### 3.3.2. Importance of Adsorption on Reaction Kinetics

What is known from the work on photocatalysis so far is that pre-adsorption of reactants on the surface of TiO<sub>2</sub> during a photocatalytic reaction leads to a more efficient electron transfer process [40,41]. Our knowledge in this area continues to grow from in-situ experiments in which the surface of TiO<sub>2</sub> has been probed as the reaction proceeds [25,42–46]. Bahnemann et al. have used laser flash photolysis experiments to investigate the electron transfer kinetics to donors and acceptors. They found that the adsorption of the model compounds DCA and SCN on the TiO<sub>2</sub> surface prior to the band gap excitation was a prerequisite for efficient hole scavenging [47]. Similar studies of adsorbed oxalic acid, where more than one surface complex is built at the surface of the TiO<sub>2</sub> nanoparticles, showed that they degrade or photomineralize with different kinetic performance [48].

**3.3.2.1. Factors Affecting Adsorption.** The interaction between the TiO<sub>2</sub> surface and the adsorbant molecules, and hence adsorption, is influenced by both the adsorbant that is being degraded and the surface. With regard to the adsorbant, important properties are; functional groups, the orientation of charges or localized electronic densities, size of molecule (organic compounds), atomic radius (inorganic compounds), chain length, possibilities of binding to the surface atoms to make covalent bonds, and the possibilities to form bonds with co-adsorbed species, e.g., water, other species of the same to form dimers or oligomers. The surface properties of TiO<sub>2</sub> influencing the adsorption concentrate on the nature of the exposed crystallographic facets, e.g. the unsaturated surface atoms ready for making bonds with the adsorbant to lower the surface energy. The surrounding environment, for instance, pH, ionic strength, and the nature of the solvent are crucial for the adsorption.

**3.3.2.2. Effects of Adsorption Strength on Reaction Rates.** For pollutant molecules that are chemisorbed on TiO<sub>2</sub>, a direct reaction with the photogenerated holes is the dominant mechanism and is typically accompanied by faster reaction rates. For example, Pilkenton et al [49,50] reported that the chemisorbed alkoxide species, such as ethoxide and 2-propoxide, are more reactive than the physisorbed alcohol species. Chemisorbed molecules that chelate the Ti atom at the surface, such as catechols also promptly scavenge the photogenerated holes in TiO<sub>2</sub>. This charge-transfer reaction is very rapid and competes with the charge recombination and trapping of the photogenerated holes by other surface defects [51]. The effect of organic adsorption can be seen from studies on the charge carrier dynamics. Rothenberger reported hole capturing by OH<sup>-</sup> groups to require 250 ns [5]. Meanwhile, Tamaki and co-workers reported a hole decay within 8 ns in the presence of well adsorbed alcohols [52]. Hence, well-adsorbed organics are able to compete with surface hydroxyl groups for the valence band holes (refer to Figure 1).

The strong adsorption of the oxidized organic can however prove to be problematic for the reaction rates. For example, Tachikawa et al suggested the existence of a charge recombination between the radical cation intermediates that are surface adsorbed and conduction band electrons. This was seen to lower the quantum yield [53]. In such systems, it was observed that chemisorbed species were less reactive than the physisorbed counterparts [51]. One way to get around this may be to introduce metal ions into the

solution that would compete with the radical cations and promote their desorption process from the TiO<sub>2</sub> surface [53].

**3.3.2.3. Effect of Reactant Structure on Adsorption and Reaction Rates.** Many studies have been devoted to the examination of the link between structure, adsorption and reaction rates. As mentioned earlier, Matthews [32] found a link between reaction kinetics and the extent of adsorption. Denny et al [54] studied Pt-TiO<sub>2</sub> as photocatalysts for the degradation of a series of alcohols and carboxylic acids, and found that increasing the chain length of the target organic lowered the rates due to steric effects and formation of rate-limiting intermediates. The presence of an increased number of hydroxyl groups in aliphatic compounds led to an increase in reaction rates of hydroxylated aliphatic compounds but not hydroxylated aromatics. Alcohols, which do not extensively adsorb on the photocatalyst, were also found not to be susceptible to the increased hole availability invoked by Pt [54]. Tamaki et al [52] proposed that the rate-limiting step for alcohol photocatalytic degradation was the hole transfer from trapping sites to the alcohol molecules. A definitive reason for the different oxidation times for different alcohols was not given. A discussion was presented on the role of ionization potentials of alcohols in alkoxy forms adsorbed on TiO<sub>2</sub>. Other factors discussed in that work were the adsorption manners of alkoxy form in particular, their orientation with respect to the surface (surface complexes), dynamical motions of the alkoxy forms, and surrounding alcohols. These latter parameters, as we pointed out earlier, are indeed of high relevance when designing an experiment for the study of kinetics and photocatalytic mechanisms. Additionally, the importance of diffusion restrictions within porous structures can also play a role [26].

**3.3.2.4. Effect of Solution pH on Adsorption and Reaction Rates.** The solution pH is also crucial in determining the extent of adsorption of the reactants and hence the observed reaction rates. The solution pH affects the degree of dissociation of organic acids (which depends on their pK<sub>a</sub>), and hence the extent of adsorption in their ionized form. The effect of pH can be interpreted in terms of electrostatic interactions between the charged TiO<sub>2</sub> particles and the contaminants to be degraded. TiO<sub>2</sub> has a point of zero charge around 6.5, and will therefore be positively charged below pH 6.5 and negatively charged above this pH. A variation in pH also affects surface speciation of TiO<sub>2</sub> due to its amphoteric nature. Under acidic or alkaline conditions the surface of titania can be protonated or deprotonated, respectively. Temperature is an additional factor to take into account at the moment of considering precise points of zero charge. Changes in temperature are sometimes useful to displace the equilibrium to a desired value suitable for establishing electrostatic interactions (attraction) with the partially or totally ionized pollutant. In general, titania photocatalytic systems in aqueous solutions are sensitive to pH adjustments due to electrostatic favored adsorption, however, electroneutral adsorption cannot be neglected being the dominant manner of adsorption of organic acids in solution. In these cases, apart from the straightforward adsorption, e.g. the entire molecule as a whole on one active site, electroneutral adsorption can also occur when the proton dissociation takes place in the very close vicinity of the surface, followed by a rapid and simultaneous chemisorption of both moieties, e.g., the H<sup>+</sup> and the deprotonated organic acid [48]. It is important to note that titania surfaces offer an optimum scenario for electroneutral adsorption since the exposed facets either of rutile (110) or anatase (100) contain dangling Ti and O atoms closed to each other at the surface [42].

**3.3.2.5. Importance of Adsorption for Photocatalytic Reduction Reactions.** Adsorption is also of critical importance for the reduction of metal ions in solution. Here, we use the example of silver ion reduc-

tion in the presence of polyvinyl alcohol (PVA) as hole scavenger to illustrate this [11]. The experimental conditions were an initial silver ion concentration of  $2 \times 10^{-4}$  mol/L,  $5 \times 10^{-3}$  mol/L PVA, 10 nm colloid  $\text{TiO}_2$  at a 0.5 g/L catalyst loading at a reaction pH of 11.5. Based on the size of  $\text{Ag}^+$  ion, each ion occupies  $1 \times 10^{-18}$  m<sup>2</sup>, therefore a maximum of 300  $\text{Ag}^+$  can be accommodated on each 10 nm  $\text{TiO}_2$  particle ( $3.14 \times 10^{-16}$  m<sup>2</sup>). At pH 11.5, with PVA in the system it is assumed that  $\text{Ag}^+$  occupied approximately 10% of the adsorption sites; therefore at pH 11.5, we have 100% adsorption of Ag ions on  $\text{TiO}_2$ . When calculating the kinetic constant, using  $k \sim 10^{14} \text{M}^{-1} \text{s}^{-1}$  (obtained from quenching of visible emission of ZnO by  $\text{Ag}^+$  [15]), the reduction of  $\text{Ag}^+$  ions is expected to occur within  $0.3 \times 10^{-10} \text{s}^{-1}$  (refer to equation 1). Therefore at pH 11.5,  $\text{Ag}^+$  reduction can compete with the recombination reaction of the electrons and the holes. This is in agreement with Iwata et al who studied the carrier dynamics of Pt- $\text{TiO}_2$  photocatalysts, by absorption spectroscopy in the near IR region [55]. For these photocatalysts the observed decay process occurred within 2.3 ps.

$$\tau = \frac{\ln 2}{C_{0\text{Ag}^+} k} = 0.3 \times 10^{-10} \text{s}^{-1} \quad (1)$$

In some cases, the adsorption of both inorganic ions (electron scavenger) and target organic (hole scavenger) is essential for optimum reaction rates. Tan and co-workers examined the photocatalytic reduction of selenate in the presence of formic acid as hole scavenger [56]. This study investigated the effect of pH, initial concentrations of formic acid and selenate ( $\text{Se(VI)}$ ) ions. The adsorption of both  $\text{Se(VI)}$  and formate ions onto  $\text{TiO}_2$  surface were shown to be essential for the reduction of  $\text{Se(VI)}$  ions to elemental selenium (Se), with a strong interplay between the effect of pH, initial reactant concentrations and the order in which the reactants were introduced into the system. On a similar system, Pichat et al [57] showed the preferential surface adsorption of Se ionas on labile (coordinatively unsaturated) surface O atoms using oxygen isotopic exchange (OEI).

**3.3.2.6. Effect of Impurities on Adsorption and Reaction Rates.** The presence of impurities and other competing adsorbed species can also play a role and affect the kinetics. Numerous studies have also been carried out to investigate the effect of impurity ions such as nitrates, sulfates and chlorides. Their effect is normally understood in terms of poisoning of the catalyst surface and blocking of active sites, however, their contribution to the photocatalytic rate may also be via direct interactions with the pollutant, e.g., changing the pollutant's structure, and charge or electronic density distribution, which affects the surface coverage. In addition, care must be taken when recycling of the catalyst is intended as was shown for the degradation of dichloroacetic acid using recycled Ag- $\text{TiO}_2$  catalysts [58]. The addition of auxiliary electron acceptors such as  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  can increase the rate of photocatalytic degradation.

### 3.3.3. Importance of Photocatalyst Structure on Reaction Kinetics

In general, two important factors in relationship to the photocatalyst structure are the surface coverage reached by the pollutant and the type of surface complexes formed on the exposed nanoparticle surfaces. The effect of the crystalline form of  $\text{TiO}_2$  definitively plays a role on the degree of adsorption of the pollutant, hence affecting the resulting kinetics [42]. Mendive et al studied the adsorption and the photoreaction of oxalic acid on the surface of  $\text{TiO}_2$ , by ATR-FTIR measurements and quantum chemical calculations and showed differences between the nature of the adsorbed structures on anatase (100) and rutile (110). Two structures were shown to adsorb on anatase  $\text{TiO}_2$  and only one adsorbed structure was observed for rutile [42]. Theoretical calculations performed by Vittadini and co-workers showed a difference between the amount

of methanol chemisorbed as methoxy form on  $\text{TiO}_2$  (001) and (101) surfaces [59].

Yamakata and co-workers [60] used time resolved IR absorption to study the charge carrier dynamics of 9 different  $\text{TiO}_2$  photocatalysts. The recombination observed in the vacuum was said to be dominated by intrinsic, bulk properties of the catalysts. The authors did not further distinguish between the influential variables. A correlation between composition and surface area was not found. This again highlights the complexity of the photocatalytic process and the interplay of a number of parameters that decide the overall reaction kinetics.

The effect of structural modification of photocatalysts with metals or dyes to increase photocatalytic activity has received a lot of attention. The dynamics of the photogenerated charge carriers in these photocatalysts provide insight into the intrinsic properties of the photocatalysts. Navio et al. showed the significance of the amount of Fe added to  $\text{TiO}_2$  for the reduction of methyl viologen ( $\text{MV}^{2+}$ ) [61]. Laser flash photolysis studies on the charge carrier dynamics of metal-doped semiconductor systems have been carried out on Ag- $\text{TiO}_2$  [11,62,63], Pt- $\text{TiO}_2$  [7,13,14,54,64] and Au- $\text{TiO}_2$  [65]. These studies demonstrated the fast kinetics (picosecond) of the transfer of electrons from  $\text{TiO}_2$  to the metal deposits. The role of metal deposits can also be understood in terms of facilitating the electron transfer to oxygen and electron hole separation.

Molecular oxygen plays an indispensable role in  $\text{TiO}_2$  photocatalysis and as can be seen in Figure 1, this is the slowest step in photocatalytic reactions, occurring on the millisecond time scale, and is seen as the rate-limiting step. Hence by enhancing the transfer of electrons to  $\text{O}_2$ , the reaction kinetics can be greatly accelerated. Additionally, oxygen generates active species such as  $\text{O}_2^-$  in the photocatalytic reactions and accelerates the mineralization of organic substances. However, electron acceptors other than oxygen are also taken into account in oxygen-free systems in order to explain the subsequent photocatalytic reactions. Finally, Friedmann et al and Lakshminarasimhan et al [11,65,66] suggested the occurrence of the antenna effect in aggregated metal- $\text{TiO}_2$  nanoparticles, whereby electronic contact within the entire network  $\text{TiO}_2$  structure is sufficient for the particles to act as efficient electron relays, enabling the charge transfer to the solute. The antenna effect has also been observed in aggregated undoped  $\text{TiO}_2$  systems [10,66].

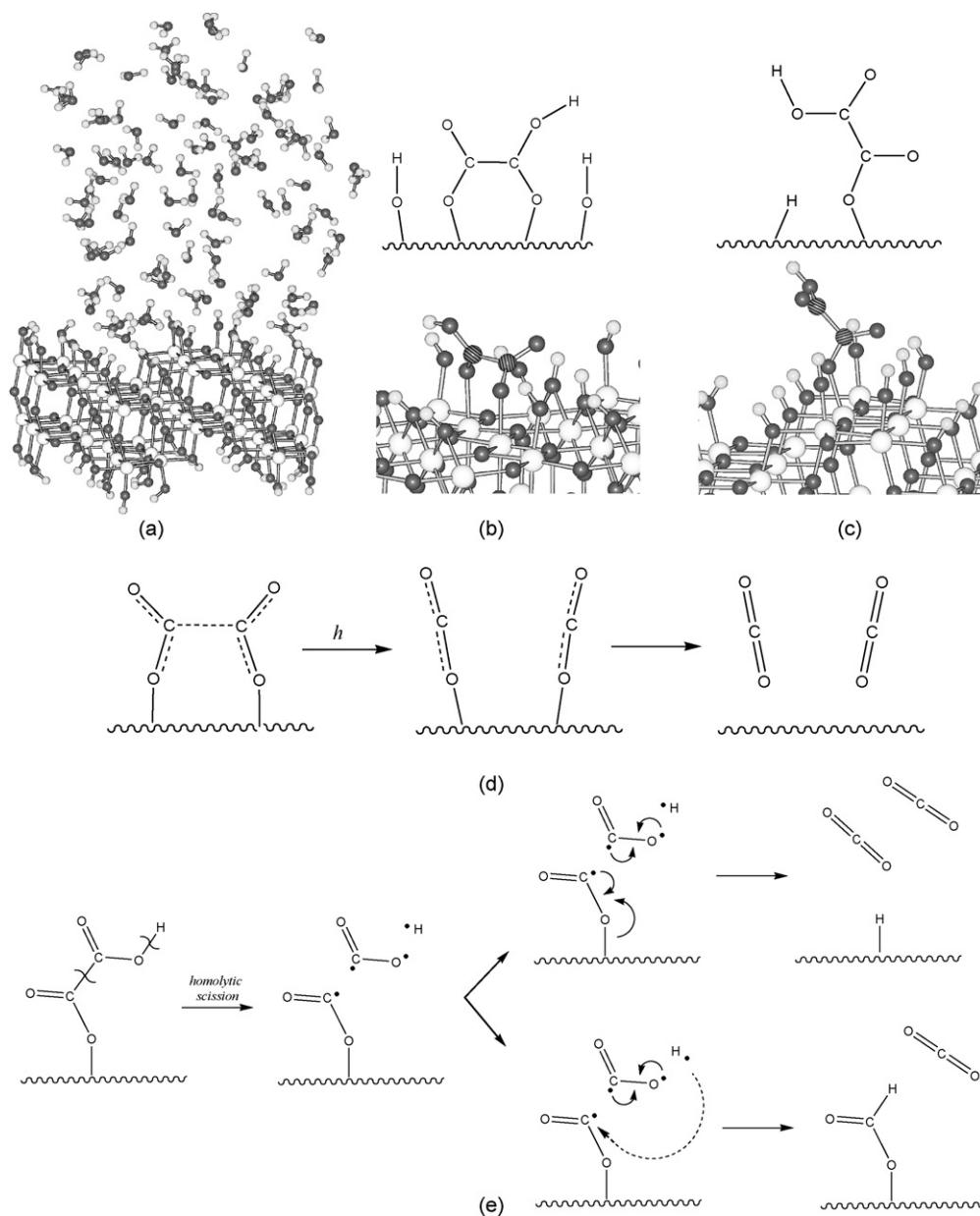
Improving the slow kinetics of visible light photocatalysis is a goal of many current research works. Particular attention has also been given to sensitized  $\text{TiO}_2$  systems (for example refer to [67,68]. N, S, and C and F doped  $\text{TiO}_2$  nanoparticles have also received considerable attention in recent years [69,70]. The low efficiency of these photocatalysts remains an issue, and a better understanding of the underlying charge carrier dynamics is needed for designing improved visible light photocatalysts. Metal ion implantation is an effective method to modify semiconductor electronic structures to improve visible light response [71]. This method introduces metal ions (accelerated by high voltage) into the  $\text{TiO}_2$  matrix. The metal ions lead to a shift in the photoresponse of the  $\text{TiO}_2$  without changing its surface properties. Such metal ion implanted  $\text{TiO}_2$  photocatalysts have been referred to as "second generation photocatalysts".

Pan et al. used self-assembly of a carotenoid and pheophytin on the surface of  $\text{TiO}_2$  to mimic the electron transfer chain in natural photosynthesis as a novel way to lengthen the lifetime of the charge carriers [72]. Composite CdS/ $\text{TiO}_2$  have shown an increase in quantum yield from 2.3% in bare  $\text{TiO}_2$  to 8.8% in CdS/ $\text{TiO}_2$  [73]. Another new approach was to coat the  $\text{TiO}_2$  surface with a thin overlayer of insulating oxides (e.g.,  $\text{Al}_2\text{O}_3$ ) that acts as a barrier layer for the recombination process [74]. This barrier had little influence on the electron injection from the dye sensitizer into  $\text{TiO}_2$ , due to the very fast dynamics of the electron injection.

An interesting approach related to the system's structure is one of Ozin and co-workers [75] where the coupling of both, the titania light absorption and the optical properties of photonic structures, are used for amplifying photocatalytic reactions rates. Slow photons arising from the slow propagation of certain frequencies through an inverted opal structure of  $\text{TiO}_2$  are responsible for the enhancement of light absorption and thus an increase of electron-hole pairs with the consequent increase in the degradation rates of the model pollutant (methylene blue). The materials are tuned to generate, upon UV irradiation, slow photons at those frequencies at the titania edge of absorption which are normally not well absorbed. Such a promising technology needs further development and much research must be carried out, opening thus the doors for new ideas and possibilities of deeper and alternative exploration of the parameters affecting the photocatalytic systems.

#### 4. Theoretical Studies: Quantum Integrated Systems

Quite a different point of view for the study of the photocatalytic systems arises from theoretical calculations carried out on such systems. In theoretical calculations, normally done by quantum chemical methods, semi-empirical [76] or totally pure ones, such as ab-initio [77] all the parameters, intrinsic and extrinsic, discussed previously, are considered at once. That is, the parameters are linked one to the other, and mainly interconnected by the unavoidable presence of the interface when using a model cluster that includes a piece of a titania nanoparticle and the pollutant in the gas phase or in solution directly in contact. If the division of extrinsic and intrinsic is established by the interface, theoretical calculations of the system as a whole consequently integrate both. For example, the local environment where a molecule or an ion is



**Figure 2.** Results from theoretical calculations with MSINDO [25,44,45] rutile (100) and anatase (100) in contact with an aqueous solution of oxalic acid. (a) 3D cluster for the simulation of the systems, an anatase cyclic cluster exposing the (100) face in contact with 100 water molecules at a liquid density, (b) and (c) the most abundant electroneutrally adsorbed oxalic acid in equilibrium in dark conditions: (b) bidentate species at rutile (110), and (c) monodentate species at anatase (100), (d) and (e) reaction mechanisms of the UV excited systems with the bidentate species (d) producing two  $\text{CO}_2$  molecules, and the homolytic scission of the excited monodentate species (e) yielding  $\text{CO}_2$  by oxidation or aldehyde by reduction.

adsorbed, which constitutes normally the entire model cluster and the maximum extent of the calculations till nowadays, is defined as a quantum integrated system, with different properties from the bare photocatalyst, or from the isolated molecule or ion in the gas phase or in solution, or from the additive contribution of both.

Theoretical calculations can be found in the literature describing the adsorption configuration of many types of adsorbants [78], either organic or inorganic, at the surface of the mostly used titania polymorphs, anatase and rutile. Within the first approach for the study of the adsorption of the chosen adsorbant, lies the complication an aqueous environment brings. Hence studies of adsorbants at the naked titania surfaces are rather abundant [79–82] while those which consider an aqueous environment are scarce [44,45]. Theoretical studies on naked surfaces are therefore comparable to adsorption experiments from the gas phase, and suitable to model, for instance, photocatalytic cases of air remediation. The consideration of the aqueous phase implies, in the case of quantum chemical calculations, a considerably increased number of atoms by the addition of water molecules simulating the aqueous environment of the pollutant. In this case, the calculation times become very long, and many times, or for some systems, some calculations are even impossible to be performed with the available computing power. However, efforts are dedicated in the present to make such calculations possible since they find, among other applications, potential to model systems for photocatalytic water treatment.

Adsorption in the dark is the first step to be investigated by theoretical studies. An example of theoretical calculations for titania photocatalysis of pollutants in aqueous solutions is given by the studies of oxalic acid on rutile and anatase [25]. The theoretical calculations in combination with ATR-FTIR results show that on both polymorphs, the adsorption of oxalic acid from the aqueous solution consists of several surface complexes of different density. While on rutile (110) a bidentate ligand is predominantly populating the surface under adsorption equilibrium [42,44], a monodentate surface complex is found to be the most abundant on anatase (100) [45].

After dark adsorption is considered, the evolution in time of the excited states as the result of the incoming irradiation of the system provides information about the subsequent reactions involving bond-breaking, new bond-formation, reduction, or oxidation. Again, the entire system is taken as a whole, and such an approach allows sometimes the distinguishing between atoms or group of atoms that are responsible for the photon absorption, e.g., which chemical entity localizes the absorption (electron-hole pair), and how these excited states are expected to evolve in the subsequent chemical reaction. For the case of oxalic acid on rutile and anatase, photocatalytic fragmentation appears as one of the most likely processes on bidentate surface complexes yielding CO<sub>2</sub>, while in monodentate species preferably bond scissions provide OH radicals which may further react with other molecules [25]. In those systems what is also observed is that some monodentate configurations do not yield bond breaking, while by the concentration of huge amounts of electronic density upon excitation, may serve as effective recombination centers (see Figure 2).

## 5. Summary and outlook

A spectrum of different organic target compounds has been studied, under a variety of conditions from simple organic or inorganic compounds to the more difficult halogenated compounds and pesticides. What is now known is that there is a strong interplay between pollutant structure, reactivity, and mode of interaction with catalyst surface. What has also become clear is that for each pollutant, a unique set of conditions may be needed for optimal performance. Although there is enough knowledge in this field to

enable successful application, a lot remains unknown and a successful result will be achieved upon a deeper understanding of the parameters taking place in every specific reaction.

Finally, of relevance are the efforts to develop standardization tests. Knowing that the reactivity of a particular catalyst is dependent on the organic being degraded, the challenge is how to develop a fair test, which organic to degrade (or classes of organics), and under what conditions. There has been an interest in the degradation of methylene blue for standardization purposes. Research efforts to address this task continue [83]. There is a much needed research effort in this area to enable the commercial viability of photocatalysis, which is potentially a green chemistry technology and would therefore be welcome.

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